# *Numerical investigations of reactive pollutant dispersion and personal exposure in 3D urban-like models*

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# Numerical investigations of reactive pollutant dispersion and personal exposure in 3D urban-like models

**Yong Zhang[1], Xia Yang[1], Hongyu Yang[1], Keer Zhang[1], Xuemei Wang[2], Zhiwen Luo[3], Jian Hang[1,4]*, Shengzhen Zhou[1]***

[1]School of Atmospheric Sciences, Guangdong Province Key Laboratory for Climate Change and Natural Disaster Studies, Sun Yat-sen University, Guangzhou, P.R. China

[2]Institute for Environmental and Climate Research, Jinan University, Guangzhou, P. R. China

[3]School of the Built Environment, University of Reading, UK

[4]National Supercomputer center in Guangzhou, P.R. China

*Corresponding author: Jian Hang, Shengzhen Zhou

Tel: +86-13710248541; +86-13710952752

E-mail address: hangj3@mail.sysu.edu.cn; zhoushzh3@mail.sysu.edu.cn

**Abstract**

With satisfactory validation by experimental data, we perform computational fluid dynamic(CFD) simulations with the standard $k$-$\varepsilon$ model to investigate how NO-$NO_2$-$O_3$ photochemistry and turbulent mixing influence reactive pollutant dispersion and vehicular $NO_x$ exposure in 21-row(neighborhood-scale~1km) three-dimensional(3D) medium-dense urban models with an approaching wind parallel(perpendicular) to the main(secondary) streets. Personal intake fraction *P_iF* and its spatially-averaged values for the entire building (i.e. building intake fraction $\langle P\_iF \rangle_B$) are adopted for reactive/passive exposure analysis with/without $NO_x$-$O_3$-photochemistry.

Some meaningful findings are proposed: 1) There are flow adjustment processes coupling turbulent mixing and chemical reactions through urban areas(i.e. secondary Street 1 to 20). NO-$NO_2$-$O_3$ photochemistry induces $O_3$ depletion and NO conversion into $NO_2$ producing significant increase in $NO_2$ exposure and slight decrease in NO exposure compared with passive dispersion. 2) With span-wise $NO_x$ sources, Street 10 in the fully-developed region experiences weaker wind and subsequently greater $\langle P\_iF \rangle_B$(0.207ppm) than Street 3(0.135ppm) in the upstream flow-adjustment region. $\langle P\_iF \rangle_B$ descends exponentially from the target building toward downstream, and Street 10 experiences quicker decay rates. 3) With stream-wise $NO_x$ sources along the main street, $\langle P\_iF \rangle_B$ first ascends, then reaches equilibrium values (e.g.0.046-0.049ppm for passive). 4) If background $O_3$ concentration [$O_3$] rises from 20ppbv to 40 and 100ppbv, more NO is oxidized by $O_3$ to generate $NO_2$. As [$O_3$]=20ppbv, if NO-$NO_2$ emission ratio decreases from 10 to 5, $NO_2$ exposure is

partly offset but NO exposure change little. Present methodologies are confirmed effective to investigate impacts of more complicated meteorological conditions and chemical mechanisms on exposure in urban districts.

**Keywords:** $NO\text{-}NO_2\text{-}O_3$ photochemistry; reactive pollutant dispersion; personal intake fraction (*P_iF*); building intake fraction ($\langle P\_iF \rangle_B$); computational fluid dynamic (CFD) simulation; three-dimensional (3D) urban models

## 1. Introduction

Following the ongoing urbanization worldwide, vehicular pollutant emissions have become one of the major sources in urban air pollution[1-3]. Heavy traffic flows, compact urban configurations and unfavorable meteorological conditions are the main reasons of large pollutant exposure and adverse health impacts on city dwellers[4]. On average, people spend more than 90% of their time indoors. Outdoor air pollutants in urban areas can penetrate into indoor via doors, windows, building cracks and other ventilation duct systems[5-7]. Particularly, vehicular pollutant exposure to urban residents living near busy roads should be paid more attention, because they suffer from higher health risks than other urban microenvironments[7-10]. Apart from reducing vehicular pollutant emissions, sustainable urban design with better understanding the influence of urban layouts and atmospheric conditions on the flow and passive/reactive pollutant dispersion in urban areas can help enhancing pollutant

dilution and mitigating traffic-related pollutant exposure[11-15].

As reviewed by the literature[16-29], in the past decades, a number of computational fluid dynamic (CFD) simulations, outdoor field observations and wind tunnel experiments have been widely performed to clarify turbulent flow characteristics and pollutant dispersion in urban models from street-scale (~100m) to neighborhood-scale (~1km). Street aspect ratios ($H/W$) are reported as the most key urban parameters in two-dimensional (2D) street canyons[16-18, 25-26, 29-32]. Realistic urban districts are usually three-dimensional (3D) with pollutant exchange across street roofs and lateral/stream-wise urban boundaries. Generally, the building planar area index $\lambda_p$ (i.e. the ratio between the planar area of buildings viewed from above and the total floor area) and the frontal area index $\lambda_f$ (i.e. the ratio of the frontal area of buildings to the total floor area) are typical building packing density indexes and key parameters of 3D urban areas[33-38]. Moreover, other significant factors have been also verified, such as building height variations[38-40], ambient wind directions[40-41], elevated building design[42-44], tree planting[46-49] etc. In addition, thermal stratification and buoyancy forces induced by wall heating and solar shading also significantly influence or dominate the flow and pollutant dispersion if wind speed is relatively small and Richardson number is large[50-56].

Recently, several researches[7, 44, 57] introduce personal intake fraction ($P\_iF$) to quantify street-scale pollutant exposure induced by vehicle emissions. In contrast to population intake fraction ($IF$) for a specific population[4, 58], $P\_iF$ is independent of population density and size which represents the fraction of pollutants inhaled

averagely by each person of a population to the total pollutant emissions. For example, 1ppm (part per million or $10^{-6}$) means the inhalation of 1mg pollutants if 1kg pollutants being emitted. By performing CFD simulations validated by experimental data, Hang et al.[7] estimated spatial mean *P_iF* (i.e. < *P_iF* >~1-5ppm) of passive pollutant (i.e. CO) in shallow 2D street canyons (*H*/*W*=0.5-1). Later, < *P_iF* > in 3D urban district models were confirmed one order smaller (~0.1ppm) than 2D models with similar aspect ratios (*H*/*W*=0.5-1)[41, 57].

Besides the dynamic dispersion of passive pollutants, there are chemical processes of reactive pollutants in urban streets, such as the $NO_x$-$O_3$ photochemistry [59-64], $NO_x$-$O_3$-VOCs chemical mechanisms[65-69] etc. Among them, the impacts of different heating scenarios and building configurations on reactive dispersion are extensively investigated through LES or RANS approaches, such as various shading settings[61], wall heating scenarios[60, 62], aspect ratios[63] etc. However, most studies so far mainly examine reactive pollutant dispersion in 2D street canyons while investigations on reactive pollutant dispersion and the related exposure in 3D urban models are still rare. Therefore, this study incorporates NO-$NO_2$-$O_3$ chemistry into CFD simulations and numerically investigates reactive pollutant dispersion and exposure in urban models. As a start, the impacts of various ground-level source locations and reactant proportions (NO:$NO_2$:$O_3$) in 3D medium-dense urban models (*H*/*W*=1, $\lambda_p$=$\lambda_f$=0.25) are studied under neutral meteorological conditions.

The sketch of this paper is organized as follows: Section 2 introduces the indexes for pollutant dispersion and exposure. Section 3 illustrates model setups and all test

cases in CFD simulations. Section 4 presents the flow and pollutant dispersion validations by wind tunnel data. Section 5 shows results and discussions, and Section 6 draws the conclusions.

## 2. Indexes for pollutant dispersion and exposure

### 2.1 Personal intake fraction (*P_iF*) and building intake fraction (<*P_iF*>$_B$)

Population intake fraction (*IF*) and personal intake fraction (*P_iF*) are effective indexes to quantify vehicular pollutant exposure in local streets or neighborhoods[41, 44, 57]. Both exposure indexes are defined as Eq. (1):

$$IF = \sum_i^N \sum_j^M P_i \times Br_{i,j} \times \Delta t_{i,j} \times Ce_j / \dot{m} \quad (1a)$$

$$P\_iF = IF / \sum_j^M P_i \quad (1b)$$

where, $N$ and $M$ are the number of age groups and microenvironments, $P_i$ represents the population size for the age group $i$, $Br_{i,j}$ ($m^3/s$) and $\Delta t_{i,j}$ (s) are the average breathing rate and the individual time spent for the $i$th age group in the $j$th microenvironment, $Ce_j$ ($kg/m^3$) denotes pollutant concentration in microenvironment $j$ and $\dot{m}$ (kg) means total emissions released from vehicles. It is worth mentioning that *P_iF* is independent of pollutant release rates as well as population density and size, but can be influenced by building configurations, meteorological conditions and pollutant source settings etc.

According to the literature[4, 70-71], the population data are categorized into

three subgroups($N$=3, Fig. 1a): Children(21.2%), Adults(63.3%) and Elders(15.5%). Moreover, the time activity patterns for each subgroup are divided into four microenvironments($M$=4, Fig. 1b): indoors at home($j$=1), other indoor locations($j$=2), in or near vehicles($j$=3), and other outdoor locations($j$=4). Table 1 lists activity time patterns and breathing rates in each subgroup for indoors at home($j$=1). In this study, all present building models are supposed to residential type and only $j$=1 (indoors at home) is adopted to calculate *P_iF* [44, 57]. Especially, the area-averaged *P_iF* of the building wall surface is denoted as wall intake fraction($\langle P\_iF \rangle_W$). The spatially-averaged *P_iF* of the entire building surfaces is represented as building intake fraction($\langle P\_iF \rangle_B$), which means the fraction of total traffic emissions inhaled averagely by each person living in this roadside building.

## 2.2 Photostationary state defect ($d_{ps}$, unit: %)

Referring to previous researches[59-60], the photostationary state defect ($d_{ps}$) is an effective indicator to measure the departure degree from photochemical equilibrium and can be expressed in the following form:

$$d_{ps} = \left( \frac{k_1[\mathrm{NO}][\mathrm{O_3}]}{J_{NO_2}[\mathrm{NO_2}]} - 1 \right) \times 100 \quad (2)$$

here, $k_1[\mathrm{NO}][\mathrm{O_3}]$ and $J_{NO_2}[\mathrm{NO_2}]$ represent the depletion and generation rates of ozone. $d_{ps}$ is positive value if ozone depletion rate greater than its formation rate, and vice versa. Especially, $d_{ps}$ equals zero when chemical reactions reach equilibrium state.

## 3. CFD setups and case descriptions

### 3.1 Numerical approaches

With advances in computer technologies, CFD as a powerful modelling tool has been widely employed to reproduce turbulent flow structure as well as to predict pollutant dispersion and transport in urban districts. Though large eddy simulations (LES) have been confirmed to be more accurate in predicting turbulence than Reynolds-Averaged Navier-Stokes (RANS) models[27, 73-75], RANS approaches are still extensively used, since LES models require expensive computational expenses and have challenges in selecting sub-grid scale models and specifying appropriate boundary conditions. Moreover, among the RANS models (e.g. various $k$-$\varepsilon$ and $k$-$\omega$ models), the standard $k$-$\varepsilon$ model shows good agreements with experimental data and has been widely adopted[7-8, 37-38, 45, 57-58, 76-79], although it has limitations in predicting turbulent kinetic energy in strong-wind regions. Therefore, by considering model performance and computational loads, the standard $k$-$\varepsilon$ model is selected to solve the steady-state isothermal flow field. The governing equations for the flow and turbulent quantities implemented are as below[80]:

The mass continuity equation:

$$\frac{\partial \overline{u}_j}{\partial x_j} = 0 \tag{3}$$

The momentum equation:

$$\overline{u}_j \frac{\partial \overline{u}_i}{\partial x_j} = -\frac{1}{\rho}\frac{\partial \overline{p}}{\partial x_i} + \frac{\partial}{\partial x_j}\left(\nu \frac{\partial \overline{u}_i}{\partial x_j} - \overline{u_i' u_j'}\right) \quad (4)$$

The transport equations of turbulent kinetic energy ($k$) and its dissipation rate ($\varepsilon$):

$$\overline{u}_i \frac{\partial k}{\partial x_i} = \frac{\partial}{\partial x_i}\left[\left(\nu + \frac{\nu_t}{\sigma_k}\right)\frac{\partial k}{\partial x_i}\right] + P_k - \varepsilon \quad (5)$$

$$\overline{u}_i \frac{\partial \varepsilon}{\partial x_i} = \frac{\partial}{\partial x_i}\left[\left(\nu + \frac{\nu_t}{\sigma_\varepsilon}\right)\frac{\partial \varepsilon}{\partial x_i}\right] + C_{\varepsilon 1}\frac{\varepsilon}{k}P_k - C_{\varepsilon 2}\frac{\varepsilon^2}{k} \quad (6)$$

where, $\overline{u}_j$ is mean velocity components ($\bar{u}_j = \bar{u}, \bar{v}, \bar{w}$ as $j$=1, 2, 3); $\nu$ and $\nu_t = C_\mu \frac{k^2}{\varepsilon}$ ($C_\mu$=0.09) represent the kinematic viscosity and the eddy viscosity, respectively; the Reynolds stress tensor $-\overline{u_i' u_j'}$ and the turbulence production term $P_k$ are defined as:

$$-\overline{u_i' u_j'} = \nu_t\left(\frac{\partial \bar{u}_i}{\partial x_j} + \frac{\partial \bar{u}_j}{\partial x_i}\right) - \frac{2}{3}k\delta_{ij} \quad (7)$$

$$P_k = \nu_t \times \frac{\partial \overline{u}_i}{\partial x_j}\left(\frac{\partial \overline{u}_i}{\partial x_j} + \frac{\partial \overline{u}_j}{\partial x_i}\right) \quad (8)$$

Note that $\delta_{ij}$ is the Kronecker delta whose value is 1 when $i$=$j$ and otherwise is 0.

The $NO_x$-$O_3$ simple photochemical mechanism is described as follows[59-60]:

$$NO_2 + h\nu \rightarrow NO + O \ , \qquad J_{NO_2} \quad (9a)$$

$$O + O_2 + M \rightarrow O_3 + M \ , \qquad k_2 \quad (9b)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \ , \qquad k_1 \quad (9c)$$

Here, $M$ denotes a third molecule, for example $O_2$ or $N_2$, to absorb excess energy and stabilize $O_3$ molecule formed; $J_{NO_2}$, $k_2$ and $k_1$ represent rate constant for each reaction, respectively. Since the oxygen atom (O) is highly reactive, it combines rapidly with $O_2$ once O is produced from $NO_2$ photolysis. This is so-called pseudo-steady-state approximation that the depletion and production rates of $O_3$ are

nearly equal[81]:

$$k_2[\mathrm{O}][\mathrm{O_2}][\mathrm{M}]=J_{NO_2}[\mathrm{NO_2}] \quad (10)$$

Therefore, Eq. (9a) is the rate control step for $O_3$ formation. Based on the above assumption, the transport equations for reactive pollutants can be defined as[59-60]:

$$\overline{u}_j\frac{\partial[\mathrm{NO}]}{\partial x_j}=D_m\frac{\partial^2[\mathrm{NO}]}{\partial x_j\partial x_j}+\frac{\partial}{\partial x_j}\left(D_e\frac{\partial[\mathrm{NO}]}{\partial x_j}\right)+J_{NO_2}[\mathrm{NO_2}]-k_1[\mathrm{O_3}][\mathrm{NO}]+S_{NO} \quad (11a)$$

$$\overline{u}_j\frac{\partial[\mathrm{NO_2}]}{\partial x_j}=D_m\frac{\partial^2[\mathrm{NO_2}]}{\partial x_j\partial x_j}+\frac{\partial}{\partial x_j}\left(D_e\frac{\partial[\mathrm{NO_2}]}{\partial x_j}\right)-J_{NO_2}[\mathrm{NO_2}]+k_1[\mathrm{O_3}][\mathrm{NO}]+S_{NO_2} \quad (11b)$$

$$\overline{u}_j\frac{\partial[\mathrm{O_3}]}{\partial x_j}=D_m\frac{\partial^2[O_3]}{\partial x_j\partial x_j}+\frac{\partial}{\partial x_j}\left(D_e\frac{\partial[\mathrm{O_3}]}{\partial x_j}\right)+J_{NO_2}[\mathrm{NO_2}]-k_1[\mathrm{O_3}][\mathrm{NO}] \quad (11c)$$

where, $D_m$ and $D_e$ are the molecular and eddy diffusivity; the third terms on the right-hand side of Eq. (11) represent chemical reaction term; $S_{NO}$ and $S_{NO_2}$ denote the source terms of NO and $NO_2$; the Schmidt number $Sc_t=\nu_t/D_e$ is specified as 0.7[33, 39, 46, 48, 78]. Furthermore, the photolysis rate $J_{NO_2}$ and rate constant $k_1$ are calculated by [59-60]:

$$J_{NO_2}=8.14\times10^{-3}\left\{0.97694+8.3700\times10^{-4}(T\text{-}273.15)+4.5173\times10^{-6}\times(T\text{-}273.15)^2\right\} \quad (12a)$$

$$k_1=4.405\times10^{-2}exp(-\frac{1370}{T}) \quad (12b)$$

Here, $T$ is temperature in K; the units of $J_{NO_2}$ and $k_1$ are $s^{-1}$ and $ppbv^{-1}s^{-1}$. Additionally, the temperature-dependent rate constant is not considered in isothermal flow of this study, thus $J_{NO_2}$ and $k_1$ are $8.1\times10^{-3}$ $s^{-1}$ and $4.450\times10^{-4}$ $ppbv^{-1}s^{-1}$ by assuming reactive pollutants undergo chemical processes under the isothermal condition with a fixed $T$ of 298.15K.

All governing equations(Eqs. (3-6, 11)) are discretized by a finite volume method (FVM) with the second-order upwind scheme. The SIMPLE algorithm is employed for pressure and velocity coupling. The under-relaxation factors for pressure, momentum, $k$ and $\varepsilon$ terms are specified as 0.3, 0.7, 0.8 and 0.8. Numerical simulation does not stop until the absolute residuals of all variables are less than $10^{-6}$.

### 3.2 Three-dimensional (3D) urban model setups in CFD

The building layouts, as depicted in Fig. 2a, are based on the idealized 3D medium-dense urban clusters (i.e. street aspect ratio $H/W$=1; building packing density $\lambda_p=\lambda_f$=0.25). To better illustrate model configurations, $x$, $y$ and $z$ are described as the stream-wise, span-wise and vertical directions, respectively. The cubic building models($H=B$=30m) with a uniform spacing($W_s=W_m$=30m) are constructed in $x$ and $y$ directions. Moreover, the approaching wind is parallel to the main streets($x$ direction) and perpendicular to the secondary streets($y$ direction). $x/H$=0 means the cross section in windward street opening and $y/H$=0 denotes the central cross section of the main street (Fig. 2c).

As verified by the literature[38-40, 82-83], the airflow in the middle column is hardly affected by lateral boundaries if the lateral width of the urban model is sufficiently large. Hence, only half of the middle column with two lateral symmetry boundaries are considered during CFD simulations to reduce computational efforts (Fig. 2b). Following the CFD guidelines[84-86], the distances between urban

boundaries and the domain top, domain inlet, domain outlet are 9*H*, 6.7*H* and 32.3*H*, respectively. Furthermore, the zero normal gradient boundary condition is adopted at two lateral boundaries and the domain top (i.e. symmetry) and the domain outlet (i.e. outflow). Several recent studies[5-6, 8-9, 44, 57-58] reported that, pollutant concentration on the wall surfaces of near-road buildings can be treated as indoor concentration originated from outdoor pollutants since the indoor/outdoor (I/O) ratio of pollutant concentration is nearly one for naturally-ventilated buildings[5, 72]. Therefore, by assuming all present building models are naturally-ventilated type, the flow and pollutant dispersion within indoor space of buildings are not taken into account to reduce the grid numbers and computational costs in CFD simulations. The literature have applied such technique to effectively quantify vehicular pollutant exposure in 2D street canyons or 3D urban models[5-6, 8-9, 44, 57-58].

For the domain inlet, the power-law time-averaged velocity profile $U_0(z)$ in the upstream free flow is adopted (Eq. 13a)[40-41, 57, 82-83] which is scaled to that in wind tunnel experiments[87]. Base on the CFD guideline[84-86], vertical profiles of $k(z)$ and $\varepsilon(z)$ are given by Eqs. (13b-c):

$$U_0(z)=U_{ref}\times(z/H)^{0.16} \tag{13a}$$

$$k(z)=u_*^2/\sqrt{C_\mu} \tag{13b}$$

$$\varepsilon(z)=C_\mu^{3/4}k^{3/2}/(\kappa_v z) \tag{13c}$$

where, $U_{ref}$ is the reference velocity at the building height in upstream free flow ($U_{ref}$=3.0 m/s at $z$ =$H$); the friction velocity $u_*$=0.24m/s[40-41, 57, 82-83]; von

Karman constant $\kappa_v$=0.41, $C_\mu$=0.09. Furthermore, vertical profiles of Eq. (13) represent neutral atmospheric boundary layer with a full-scale surface roughness $z_0$=0.1m[93] and have been adopted in previous studies[40-41, 57, 82-83].

In addition, Fig. 2c demonstrates the overhead and lateral views of mesh distribution for test cases. The minimum grid size of 0.2 m near the wall surfaces and the stretching ratio between adjacent grids of 1.15 (about 3.2 million hexahedral cells) are applied to ensure sufficiently fine grid at the pedestrian level (0-1.5m) and near building surfaces. As the normalized distance $y^+$ ($y^+=yu_\tau/v$) ranges from 30 to 600 at most regions of wall surfaces, standard wall function with no slip boundary condition is set on all wall surfaces. According to the literature[13, 40, 88-89], a specific roughness modification is assigned to the upstream and downstream ground to obtain a horizontally homogeneous ABL surrounding urban regions. Especially, the grid independence tests are presented later in subsection 4.1.

### 3.3 Pollutant source settings and model description of test cases

Three kinds of pollutant source locations are considered in this study, i.e. the span-wise ($y$ direction) emission sources in the 3$^{rd}$ or 10$^{th}$ secondary street is denoted as S3 and S10 (Fig. 3a-b), and the stream-wise ($x$ direction) emission sources along the main street is represented by Sm (Fig. 3c). The reactive pollutants involved in present photochemistry are NO, $NO_2$ and $O_3$. Among them, $NO_x$ is assumed to be emitted from vehicles into the street canyon while background $O_3$ concentration is

271 specified at the domain inlet and entrained by approaching wind into urban districts.
272 The background concentrations for NO and $NO_2$ at the domain inlet are zero in this
273 study. Following the literature[59-60], typical automobile emission ratio of NO to
274 $NO_2$ ($R_{NO/NO_2}$) of 10 is adopted. NO and $NO_2$ are released from the lowest grid cell
275 ($z$=0-0.2m) at rates of 100 and 10 ppbv $s^{-1}$, which corresponds to emission strengths
276 of $1.227\times10^{-7}$ and $1.88\times10^{-8}$ kg $m^{-3}s^{-1}$ ($P$=1 atm, $T$=298.15K). For S3 or S10 sources,
277 as the street width ($W_s$) is 30m, this $NO_x$ emission intensity of 849 μg $m^{-1}s^{-1}$ is
278 equivalent to a traffic volume of about 6100 vehicles per hour when considering a
279 $NO_x$ emission of 0.5g $km^{-1}$ per vehicle[59-60]. Particularly, we are mainly concerned
280 with the proportion among NO and $NO_2$ rather than the assigned emission rate for
281 each vehicular pollutant.

282 Furthermore, four $O_3$ background concentrations (i.e. [$O_3$] =1, 20, 40 and 100
283 ppbv) with $R_{NO/NO_2}$=100:10 are investigated to study the effects of different [$O_3$] on
284 reactive dispersion. In addition, Carslaw[90] verified that there is an increasing
285 $NO_2/NO_x$ emission ratio in road traffic emissions referring to observation in real cities.
286 Thus, three emission ratios of NO to $NO_2$ (i.e. $R_{NO/NO_2}$=100:10, 50:10 and 100:20)
287 with [$O_3$]=20ppbv are considered to examine the impacts of various $R_{NO/NO_2}$ on
288 reactive pollutant dispersion.

289 Overall, total 11 test cases are described as Case P [Source, $R_{NO/NO_2}$] or Case R
290 [Source, $R_{NO/NO_2}$, [$O_3$]] and summarized in Table 2. Here 'P' means passive dispersion
291 without chemical reactions, 'R' denotes reactive dispersion with NO-$NO_2$-$O_3$
292 chemistry; 'Source' contains three pollutant source locations, i.e. S3, S10 and Sm,

293 respectively; $R_{NO/NO_2}$ represents the emission ratios of NO to $NO_2$; $[O_3]$ is
294 background $O_3$ concentration (mole fraction, unit: ppbv).

295

296 **4 Validation study of flow and pollutant dispersion in 3D urban models**

297 **4.1 Flow validation by wind tunnel data**

298 In this subsection, the performances of various steady *k*-*ε* models (standard,
299 RNG and Realizable) with standard wall function are evaluated by wind tunnel data.
300 Moreover, the grid independence tests are also implemented.

301 As shown in Fig. 4a-b, idealized 3D urban models in wind tunnel experiment[87]
302 consist of 7 rows and 11 columns of regularly-aligned cubic buildings
303 ($H$=$B$=$W$=15cm). Vertical profiles of velocity components ($\overline{u}$, $\overline{w}$) and turbulence
304 kinetic energy ($k$) are measured at points of $V_i$ ($i$=1-6), which are central positions in
305 the $i$th secondary street located at $y/H$=1 and $x/H$=1.5$H$, 3.5$H$, 5.5$H$, 7.5$H$, 9.5$H$,
306 11.5$H$ respectively (Fig. 4a-b).

307 In CFD validation study, the similar full-scale model configurations
308 ($H$=$B$=$W$=30m, Fig. 4c) are reconstructed with the scale ratio of 200:1 to
309 wind-tunnel-scale models. Moreover, all CFD setups including computational
310 domains, boundary conditions and convergence criteria in this full-scale CFD
311 validation study are similar with those in subsection 3.2 except that the distance
312 between urban boundaries and domain outlet is 40.3$H$(Fig. 4c). Based on the building
313 height($H$=0.15m or 30m) and reference velocity($U_{ref}$=3m/s), the reference Reynolds

number $Re=\frac{U_{ref}H}{v}\approx30000$ and $6\times10^6$ for wind-tunnel-scale and full-scale urban models, which are much larger than 11000 satisfying Reynolds number independence requirement. Furthermore, Fig. 4d depicts the coarse, medium and fine grid arrangements with hexahedral cells of about 1, 2 and 3.3 million and the minimum grid size of 0.4m, 0.2m and 0.1m, respectively.

Fig. 5 first shows results of grid independence test at V1(Fig. 5a-b), then depicts vertical profiles of time-averaged stream-wise velocity $\bar{u}(z)$ at Points V1, V4 and V6 (Fig. 5c-e), vertical velocity $\bar{w}(z)$ (Fig. 5f) and turbulence kinetic energy $k(z)$ (Fig. 5g) at Point V1 between numerical results and experimental data. There is little difference in numerical results between the coarse, medium and fine grid, and thus medium grid is selected for case studies to reduce computational loads. Besides, the standard $k$-$\varepsilon$ model with the medium grid shows better agreements with wind tunnel data than the RNG and Realizable $k$-$\varepsilon$ models.

To further quantify the modeling accuracy and reliability of the standard $k$–$\varepsilon$ model with the medium grid arrangement, several statistical performance metrics are applied, including the mean value, the standard deviation, the factor 2 (FAC2), the normalized mean square error (NMSE), the fraction bias (FB) and the correlation coefficient (R)[91]. Among which, the closer NMSE value to zero, the smaller difference between experiment data and CFD results; FAC2 value larger than one means over-prediction against experiment data while smaller than one represents under-prediction; Similarly, the negative and positive FB values denote overestimation and underestimation. Results of $\bar{u}(z)$ at Points V1, V4 and V6 as well

as $\overline{w}(z)$ and $k(z)$ at Point V1 are listed in Table 3. Referring to COST Action 732's recommended criteria[91], a credible CFD model should satisfy the following statistical metrics standards: $0.5 \leqslant \mathrm{FAC2} \leqslant 2$, $\mathrm{NMSE} \leqslant 1.5$ and $-0.3 \leqslant \mathrm{FB} \leqslant 0.3$. Overall, metrics lie in the recommended criteria, particularly values of $\overline{u}(z)$ meet well. However, values of $\overline{w}(z)$ and $k(z)$ reveal relatively poorer performance than those of $\overline{u}(z)$, which is largely attributed to the limitation of the standard $k$-$\varepsilon$ model. Conclusively, the validation study shows that present CFD methodologies applying standard $k$-$\varepsilon$ model with medium grid have credible numerical accuracy in predicting urban turbulent flow and can be employed for further case studies.

### 4.2 Validation of pollutant dispersion by wind tunnel data

Experimental and numerical studies have been extensively performed to investigate passive pollutant dispersion in the idealized street canyons. Unfortunately, there are currently little experimental data to directly validate the present CFD model coupled with chemistry[59-60, 63-64]. However, the reactive pollutants considered in this paper are effectively passive and can be divided into two subsets, i.e. total nitrogen oxide ($NO_x$=NO+$NO_2$) and total oxidant (OX=$NO_2$+$O_3$), since reactions (Eq. 9) interconvert NO with $NO_2$, and $O_3$ with $NO_2$ but without redundant productions. In addition, the chemical reaction terms cancel out when Eqs. (11a-b) and Eqs. (11b-c) are added, which indicates that the transport and dispersion of $NO_x$ and OX can be deemed as passive scalar. Consequently, in this subsection, Standard $k$-$\varepsilon$ model with

standard wall function has been implemented and validated against wind tunnel experiment to evaluate the reliability of numerical simulation in predicting passive pollutant distribution.

The configurations of the wind tunnel measurement[92], as depicted in Fig.6a-b, are consisted of nine rectangular building models ($Lx$=27.6cm, $Ly$=18.4cm, $H$=8cm) with three rows and three columns (3×3) and uniform street widths ($W$=8cm, $H/W$=1). Moreover, tracer gas($C_2H_6$) is released from a line source (0.5cm in width, $dx$ and 18.4 cm in length, $Ls$) at a velocity of $w_{source}$=0.01 m/s which is paralleled with $y$ direction and locates in the central street canyon in front of building No.2(Fig. 6a-b). Furthermore, $C_2H_6$ concentration profiles are measured in the middle of leeward and windward walls near the line source as well as on the central line of roof surface in the building No.2(Fig. 6a-b).

In full-scale pollutant dispersion validation study, similar model configurations ($Lx$=138m, $Ly$=92m, $H$=40m, in Fig. 6c) are rebuilt with the scale ratio of 500:1 to wind-tunnel-scale models. CFD setups are similar with subsection 3.2, but the distances between urban boundaries and the domain top, domain side, domain inlet, domain outlet are 9$H$, 5$H$, 5$H$ and 15$H$, respectively. The approaching wind is parallel to the main streets($x$ direction) and perpendicular to the secondary streets($y$ direction). Furthermore, vertical profiles of stream-wise velocity $\bar{u}(z)$, turbulence kinetic energy $k(z)$ and turbulent dissipation rate $\varepsilon(z)$ fitted by measured data in wind tunnel experiments[92] are adopted at the domain inlet (Fig. 6d-f). In addition, to compare CFD results with measured data, the normalized $C_2H_6$ concentration $K$ is defined as

379 below:

380 $$K=CHU_{ref}/w_{source}dx \quad (14)$$

381 Here the height of building ($H$), the reference velocity ($U_{ref}$) and the line source
382 emission strength ($w_{source}$, $dx$) are applied.

383 As shown in Fig. 7, the agreements of $K$ between wind tunnel data and CFD
384 results are well confirming the standard $k$-$\varepsilon$ model has sufficient modeling accuracy in
385 predicting passive pollutant dispersion within 3D urban district models.

386

387 ## 5 Results and discussion

388 ### 5.1 Flow patterns in 3D urban district models

389 Fig. 8a depicts velocity distribution in the plane of $z$=1.5m (the pedestrian level).
390 Obviously, the flow adjustment process can be observed through the entire building
391 clusters, in which wind speed decreases toward downstream from Street 1 to Street 6,
392 and then reaches a comparatively flow equilibrium from Street 7 to Street 18. Fig.
393 8b-c further depict velocity magnitude and 2D streamlines in the plane of $y$=30m (the
394 center plane of the target street canyon) and $z$=1.5m for Street 3 and Street 10.
395 Moreover, the corresponding 3D streamlines are displayed in Fig. 8d. For both street
396 units, 3D downward helical vortices are produced inside the secondary streets (Fig.
397 8b-d). The lateral flow direction near street ground (i.e. $z$=1.5m) are from the
398 secondary streets to the main streets and from the downwind building (No.4 and 11)

399 to upwind building (No. 3 and 10) (Fig. 8c). In addition, Street 3 apparently
400 experiences greater wind speed than Street 10.

401 In particular, the following analysis (subsection 5.3) emphasizes more on
402 reactive pollutant dispersion in the fully-developed region (e.g. Street 10) than the
403 flow-adjust region (e.g. Street 3).

404

405 **5.2 Impacts of source locations (S3, S10 and Sm) on reactive pollutant dispersion**

406 This subsection considers the impacts of source locations (i.e. S3, S10 and Sm in
407 Fig. 3) on reactive pollutant dispersion(with chemical reactions, R-type) under the
408 specific pollutant proportion (i.e. $R_{NO/NO_2}$=100:10, [$O_3$]=20ppbv). Because the present
409 photochemical mechanism contains the interconversion of nitrogen oxides(i.e.
410 $NO_x$=NO+$NO_2$) and oxidants (i.e. OX=$NO_2$+$O_3$), The following discussions
411 (subsection 5.2 and 5.3) concentrate more on $NO_2$ to simplify analysis. Moreover,
412 passive dispersion (without chemical reactions, P-type) are also presented to
413 investigate the sole role of turbulent mixing.

414

415 **5.2.1 $NO_2$ concentration distribution in 3D urban-like models**

416 Fig. 9a-d exhibit $NO_2$ concentration between P-type(passive, left) and R-type
417 (reactive, right) cases in $y$=30m and $z$=1.5m for Street 3 and 10 fixed with span-wise
418 sources(i.e. S3 and S10). Moreover, Fig. 9e compares $NO_2$ concentration at the

pedestrian level between passive and reactive cases with $NO_x$ sources along main streets (i.e. Sm). For passive dispersion with S3 or S10 sources (P-type), due to source emissions and turbulent transports, $NO_2$ concentration near the upwind building (No.3 and 10) is higher than that near the downwind building(Fig. 9a-b). Furthermore, a large amount of $NO_2$ pollutants accumulate in the intersection of main street and secondary street(Fig. 9c-d). In an overall view, $NO_2$ concentration in Street 10 is slightly higher than Street 3. For P-type case with Sm sources(Fig. 9e), $NO_2$ concentration first rises toward downstream streets, then reaches an approximate equilibrium from Street 7 to 18. Such findings are similar with the flow adjustment as discussed in subsection 5.1.

With chemical reactions, as verified by Fig. 9, $NO_2$ concentration in R-type cases considerably exceeds that in P-type cases. Oppositely, passive NO concentration is higher than that in R-type cases.

### 5.2.2 $d_{ps}$ distribution in Street 3 and 10

Fig. 10 shows $d_{ps}$ distribution in $y$=30m and $z$=1.5m in local target streets with S3 and S10 sources. Here, the distribution of photostationary state defect($d_{ps}$) is emphasized below the roof level ($z/H$<1) and toward downstream domains (i.e. $x/H$>5 and $x/H$>19 for Street 3 and 10, respectively).

As introduced in subsection 2.2, smaller $d_{ps}$ value represents the less departure degree from photochemical equilibrium. In the centre plane of secondary streets

(*y*=30m, Fig. 10a), the local small $d_{ps}$ values emerge near the roof of the upwind building (No.3 and 10) while the large $d_{ps}$ values appear near the roof of the downwind building (No.4 and 11) and the ground level close to $NO_x$ emissions. At the pedestrian level(Fig. 10b), downstream areas of the main streets (*x*/*H*>6 and *x*/*H*>20) experience small $d_{ps}$ values while the junction regions of the main street and secondary street near $NO_x$ source locations obtain large $d_{ps}$ values, particularly in Street 3. In summary, $d_{ps}$ value is usually smaller in regions with weaker wind and turbulence, where reactive pollutants have more time to mix and react.

### 5.2.3 Concentration, $\langle P\_iF \rangle_W$ and $\langle P\_iF \rangle_B$ on building wall surfaces

Based on spatial mean concentration at the entire building surfaces, we calculate wall intake fraction($\langle P\_iF \rangle_W$) and building intake fraction($\langle P\_iF \rangle_B$) to analyze overall vehicular pollutant($NO_x$) exposure in near-road buildings. Especially, 1ppm represents 1 mg inhaled averagely by each person living in the near-road building if 1kg pollutants emitted out.

Fig. 11a-b first compare $NO_2$ concentration on the leeward and windward walls between P-type and R-type cases in target street units with S3 and S10 sources. No matter with or without chemical reactions, $NO_2$ concentrations on the leeward wall are always higher than those on the windward wall. Once $NO_x$-$O_3$ photochemical reactions are conducted, an increase of $NO_2$ concentration emerges on the upwind and downwind walls. Such results are similar with the aforementioned discussion in

461 subsection 5.2.1.

462 Then, Table 4 lists $<P\_iF>_W$ of NO and $NO_2$ at leeward and windward walls
463 adjoining target street in cases with S3 and S10 (positions as described in Fig. 3a-b).
464 Obviously, in both P-type and R-type cases, $<P\_iF>_W$ of $NO_x$ at leeward wall(Table 4,
465 row 1-4, column 2-3) are greater than those at windward wall(Table 4, row1-4,
466 column 4-5). Regarding P-type cases as the references, $<P\_iF>_W$ of $NO_2$ in R-type
467 cases rise nearly 90%-160%, i.e. 0.660 to 1.372ppm and 0.853 to 1.643ppm at
468 leeward wall for S3 and S10(Table 4, column 2), 0.180 to 0.473ppm and 0.230 to
469 0.610ppm at windward wall for S3 and S10(Table 4, column 4); while $<P\_iF>_W$ of
470 NO reduces about 9%-16%, i.e. 0.660 to 0.588ppm and 0.853 to 0.775ppm at leeward
471 wall for S3 and S10(Table 4, column 3), 0.180 to 0.151ppm and 0.230 to 0.193ppm at
472 windward wall for S3 and S10(Table 4, column 5). Because $NO_x$ emission ratio
473 released from vehicles is $R_{NO/NO_2}$=10, the present photochemical processes lead to a
474 significant increase in $NO_2$ exposure and a slight decrease in NO exposure.

475 Furthermore, $NO_2$ concentrations on the entire building wall surfaces with Sm
476 sources are presented in Fig. 11c. Both P-type and R-type cases experience the $NO_2$
477 concentration adjustment processes toward downstream buildings. To quantify $NO_x$
478 exposure adjustments in P-type and R-type cases with various sources (S3, S10 and
479 Sm), the horizontal profiles of building intake fraction $<P\_iF>_B$ of NO and $NO_2$ are
480 shown in Fig. 12. It is found that $<P\_iF>_B$ with S3 or S10 sources descends
481 exponentially toward downstream buildings(Fig. 12a-b), instead, $<P\_iF>_B$ with Sm
482 sources first ascends quickly from building No.1 to 8, then reaches an approximate

equilibrium(Fig. 12c). Besides, R-type cases experience larger $NO_2$ exposure than P-type cases, i.e. 0.420-0.108ppm against 0.135-0.020ppm for S3(Fig. 12a), 0.605-0.160ppm against 0.207-0.030ppm for S10(Fig. 12b), 0.005-0.090ppm against 0.002-0.049ppm for Sm(Fig. 12c). Oppositely, NO exposure in P-type cases are greater than R-type cases, i.e. 0.135-0.020ppm than 0.106-0.010ppm for S3(Fig. 12a), 0.207-0.030ppm than 0.168-0.017ppm for S10(Fig. 12b) and 0.002-0.049ppm than 0.002-0.045ppm for Sm(Fig. 12c).

In addition, the decay function expressed in $<P\_iF_n>_B = a \times <P\_iF_t>_B \times e^{(t-n)/b}$ is employed to further quantify the $<P\_iF>_B$ decay processes from target building unit ($t$ =4 or 11) toward downstream building ($n$=$t$ to 21) in S3 and S10 cases. Note that, smaller decay factor $b$ means relatively sharper descending processes of $<P\_iF>_B$ curves. Table 5 summarizes the $<P\_iF_t>_B$ of building "No.$t$" and the exponential decay factors $b$ in S3 and S10 cases. Obviously, compared with those in P-type case ($b$=7.46 and 3.96 in Table 5, row 1 and 3), R-type cases with S3 and S10 obtain larger $b$ for $NO_2$ (10.80 and 6.84 in Table 5, row 2 and 4) and smaller $b$ for NO (5.92 and 2.91). Moreover, $<P\_iF>_B$ curves in S10 cases(Table 5, row 3-4) decline more sharply toward downstream regions than S3 cases(Table 5, row 1-2). Particularly, as shown in Fig. 12c, $<P\_iF_t>_B$ in Sm cases are calculated by the mean $<P\_iF>_B$ from building No.9 to 21, i.e. 0.048ppm in P-type case, 0.044ppm and 0.088ppm in R-type case for NO and $NO_2$.

In summary, with $R_{NO/NO_2}$ =100:10 and [$O_3$] =20ppbv, the present $NO_x$-$O_3$ titration interactions result in the production of $NO_2$ and depletion of $O_3$ and NO. By

505 focusing on $\langle P\_iF_t \rangle_B$ values, $NO_2$ exposure in R-type cases are greater than P-type
506 cases about 3.1 times for S3, 2.9 times for S10 and 1.8 times for Sm while NO
507 exposure in R-type cases are nearly 21%, 19% and 8% smaller than P-type cases for
508 S3, S10 and Sm, respectively.

509

510 **5.3 Impacts of reactant proportions** ($NO:NO_2:O_3$) **on reactive pollutant dispersion**

511 In this subsection, based on S10 sources, we discuss the effects of different
512 reactant proportions ($NO:NO_2:O_3$) on the interaction of turbulent mixing and
513 photochemical processes in urban districts. Additionally, *P_iF* and $\langle P\_iF \rangle$ are
514 independent on source emission strength in passive pollutant dispersion, therefore
515 Case P[S10,100:10] is treated as the reference case to compare with the cases with
516 other reactant proportions.

517

518 **5.3.1 Impacts of $O_3$ background concentration ($[O_3]$)**

519 With the same emission ratio of NO to $NO_2$ (i.e. $R_{NO/NO_2}$=100:10), the impacts of
520 four $O_3$ background concentrations(i.e. $[O_3]$ =1, 20, 40 and 100ppbv) on reactive
521 pollutant dispersion are examined.

522 It is apparent that the formation of NO by photolyzing $NO_2$ is slightly dominant in
523 photochemistry when $[O_3]$ is 1ppbv. In contrast to the reference values(0.853 and
524 0.230ppm in Table 4, row 3), $\langle P\_iF \rangle_W$ of $NO_2$ at the leeward and windward walls

525 slightly decrease(i.e. 0.816 and 0.211ppm in Table 4, row 5) while $<P\_iF>_W$ of NO
526 increase a little(i.e. 0.858 and 0.233ppm). Besides, such phenomenon is distinctly
527 observed in $<P\_iF>_B$ curves(Fig. 13) between the reference case and Case R
528 [S10,100:10,1], i.e. 0.207-0.030ppm against 0.187-0.020ppm for $NO_2$(Fig. 13a) and
529 0.207-0.030ppm against 0.209-0.031ppm for NO(Fig. 13b).

530 However, if [$O_3$] rises from 20ppbv to 40 and 100ppbv, more NO is oxidized by
531 $O_3$ to generate $NO_2$. Based on the reference values (0.853 and 0.230ppm in Table 4,
532 row 3), $<P\_iF>_W$ of $NO_2$ become about 1.9-5.2 times greater (1.643, 2.454 and
533 4.442ppm in Table 4, column 2) at leeward wall and 2.6-6.7 times larger (0.610, 0.944
534 and 1.534ppm in Table 4, column 4) at windward wall; while $<P\_iF>_W$ of NO
535 reduces approximately 9%-42% (0.775, 0.694 and 0.495ppm in Table 4, column 3) at
536 leeward wall and 16%-57% (0.193, 0.159 and 0.100ppm in Table 4, column 5) at
537 windward wall. Furthermore, Fig. 13 and Table 5 display the corresponding $<P\_iF>_B$
538 curves, $<P\_iF_t>_B$ values and decay factors $b$ under different [$O_3$]. As depicted in Fig.
539 13, compared with Case R[S10,100:10,20], Case R[S10,100:10,100] and R
540 [S10,100:10,40] obviously attain much larger $<P\_iF>_B$ of $NO_2$ (1.573-0.275 and
541 0.952-0.218ppm in Fig. 13a) and smaller $<P\_iF>_B$ of NO (0.071-0.005 and
542 0.133-0.011ppm in Fig. 13b). Additionally, both decay factors of $NO_2$ and NO are
543 smaller ($b$=6.02 and 2.33 for [$O_3$]=40ppbv, $b$=4.74 and 1.87 for [$O_3$]=100ppbv in
544 Table 5, row 6-7) than those in Case R[S10,100:10,20] ($b$=6.84 and 2.91 in Table 5,
545 row 4), which implies higher [$O_3$] induces the quicker decay of $<P\_iF>_B$ curves for
546 $NO_x$ with S10 sources toward downstream building units. By concentrating on

547 $<P\_iF_t>_B$, $NO_2$ exposure in R-type cases surpass the reference case nearly 2.9, 4.6 and
548 7.6 times for $[O_3]$=20, 40 and 100ppbv, respectively(Table 5, column 2).
549 Correspondingly, $<P\_iF_t>_B$ of NO in these $[O_3]$ cases are about 19%, 36% and 66%
550 smaller than the reference values, respectively(Table 5, column 4). It clearly indicates
551 that increasing $[O_3]$ would aggravate $NO_2$ exposure within urban clusters but is
552 conductive to the mitigation of NO exposure.

553

554 **5.3.2 Effects of emission ratio of NO to $NO_2$ ($R_{NO/NO_2}$)**

555 The effects of source emission ratios ( $R_{NO/NO_2}$=100:10, 50:10 and 100:20) on
556 reactive pollutant dispersion are investigated with the same $[O_3]$ of 20ppbv.

557 It is shown that decreasing NO or increasing $NO_2$ emissions based on the
558 reference case can mildly change the fraction of NO converting into $NO_2$. For
559 example, reducing $R_{NO/NO_2}$ from 100:10 to 50:10 and 100:20, $<P\_iF>_W$ of NO
560 varies from 0.775 to 0.744 and 0.784ppm at the leeward wall(Table 4, column 3), and
561 from 0.193 to 0.186 and 0.197ppm at windward wall(Table 4, column 5). Furthermore,
562 $<P\_iF>_W$ of $NO_2$ drops from 1.643 to 1.406 and 1.205ppm at the leeward wall(Table
563 4, column 1), and from 0.610 to 0.453 and 0.400ppm at windward wall(Table 4,
564 column 4). In addition, Fig. 14 presents $<P\_iF>_B$ curves of $NO_2$ and NO in P-type and
565 R-type cases with three NO-$NO_2$ emission ratios. Obviously, photochemical reactions
566 in these R-type cases are still dominated by the depletion of $O_3$ with NO to produce
567 $NO_2$.

As displayed in Fig. 14a and Table 5, Case R[S10,50:10,20] and R [S10,100:20,20] obtain smaller $<P\_iF>_B$ and decay factor of $NO_2$ (i.e. 0.446-0.091 ppm, $b$=5.41 and 0.384-0.088ppm, $b$=6.00) than those in Case R[S10,100:10,20] (i.e. 0.605-0.160ppm, $b$=6.84). In contrast to Case R[S10,100:10,20], $<P\_iF_t>_B$ of NO in Case R[S10,50:10,20] and R[S10,100:20,20] reduce nearly 26% and 37%. However, $<P\_iF>_B$ curves and decay factors $b$ of NO are quite close between three R-type cases, i.e. 0.172-0.018, 0.168-0.018 and 0.160-0.017ppm; $b$=3.05, 2.91 and 3.11(Fig. 14b and Table 5). It is confirmed that the decrement of $R_{NO/NO_2}$ (from 10 to 5) can partly offset $NO_2$ exposure but have much less impacts on NO exposure.

Overall, the $NO_x$-$O_3$ photochemical processes dependent on the initial proportion of reactive pollutants are toward satisfying the photostationary state relationship (i.e. $k_1[NO][O_3]=J_{NO_2}[NO_2]$).

## 5.4 Limitations and future work

Since the 3D urban district models, photochemical reactions and meteorological conditions adopted in this study are fairly simplified, the present exposure results may change if more realistic factors are taken into account, such as more realistic urban configurations(e.g. with variations of building height and street width), more complicated chemical mechanisms(e.g. VOCs-$NO_x$-$O_3$) and more realistic atmospheric conditions etc. It is worth mentioning that the chemical processes dependent on reaction rates are highly associated with the reactive pollutant

concentration and ambient air temperature. Moreover, realistic atmospheric conditions include the unsteady temporal and spatial variations of wind speed and direction as well as various atmospheric stabilities and solar radiation conditions. Thus, further unsteady CFD simulations will be performed to examine the integrated impacts of urban turbulence and solar radiation on reactive pollutant dispersion in 3D urban districts.

## 6 Conclusions

Urban residents in near-road buildings commonly suffer from high exposure risk of vehicular pollutants in which $NO_x$(NO and $NO_2$) act as primary reactive pollutants. With satisfactory full-scale CFD validation of flow and pollutant dispersion by experimental data, this study first focuses on the impact of turbulent transport combined with $NO_x$-$O_3$ photochemical reactions on reactive pollutant dispersion in neighborhood-scale(21-row, ~1km) three-dimensional(3D) medium-dense urban clusters ($H/W$=1, $\lambda_p=\lambda_f$=0.25). Ground-level emission sources of NO and $NO_2$ are considered in the presence of background $O_3$. The approaching wind is parallel to the main streets and perpendicular to the secondary streets. As a start, the influences of various source locations and reactant proportions(NO:$NO_2$:$O_3$) on pollutant dispersion are investigated under neutral meteorological condition. Personal intake fraction *P_iF*, its spatially-averaged values for a building wall($\langle P\_iF \rangle_W$) and the entire building surfaces(i.e. building intake fraction $\langle P\_iF \rangle_B$) are adopted to quantify pollutant

610 exposure with and without NO-$NO_2$-$O_3$ reactions(i.e. reactive and passive).

611 Some meaningful findings are summarized as below:

612 1) There are flow adjustment processes coupling turbulent mixing and chemical
613 reactions through urban building clusters(Street 1 to Street 20 toward
614 downstream).With span-wise sources, the secondary street of Street 10 located in the
615 fully-developed region(i.e. S10 case) experiences weaker wind and subsequently
616 greater $<P\_iF>_B$ than the secondary Street 3 located in the upstream flow-adjustment
617 region (i.e. S3 case). Consequently, in contrast to S3 case, photostationary state defect
618 ($d_{ps}$) is smaller in S10 case since reactive pollutants have more time to mix and react
619 in Street 10.

620 2) With source emission ratios of NO to $NO_2$ of 10($R_{NO/NO2}$=100:10) and
621 background $O_3$ concentration of 20ppbv([$O_3$]=20ppbv), NO-$NO_2$-$O_3$ photochemistry
622 leads to production of $NO_2$ and depletion of $O_3$ and NO, inducing a significant
623 increase in $NO_2$ exposure and a slight decrease in NO exposure when compared to
624 corresponding passive dispersion which only considers the sole role of turbulent
625 transport. With span-wise pollutant sources, 3D downward helical flows transport
626 more $NO_x$ to the leeward side, inducing much greater leeward-side $<P\_iF>_W$ than the
627 windward-side. Moreover, by defining exponential decay function expressed
628 in $<P\_iF_n>_B = a \times <P\_iF_t>_B \times e^{(t-n)/b}$, it is found that $<P\_iF>_B$ descends exponentially
629 from target building ($<P\_iF_t>_B$=0.135ppm or 0.207ppm, $t$=4 or 11 for S3 or S10) to
630 downstream buildings ($n$=$t$ to 21). Especially, $<P\_iF>_B$ curves decline more sharply

631 from Street 10 toward downstream than that from Street 3. However, if stream-wise
632 sources fixed along the main streets, $<P\_iF>_B$ first ascends quickly from building
633 No.1 to 8, then reaches approximate equilibrium values of $<P\_iF>_B$=
634 0.046-0.049ppm.

635 3) Furthermore, the $O_3$ background concentration ($[O_3]$) and source emission
636 ratios of NO to $NO_2$( $R_{NO/NO_2}$) are confirmed as key factors on $NO_x$-$O_3$ reactive
637 dispersion. The formation of NO by photolyzing $NO_2$ is slightly dominant in
638 photochemistry when $[O_3]$ is 1ppbv. However, if $[O_3]$ rises from 20ppbv to 40 and
639 100ppbv, more NO is oxidized by $O_3$ to generate $NO_2$, which would aggravate $NO_2$
640 exposure within urban clusters but is conductive to the mitigation of NO exposure.
641 Under $[O_3]$ of 20ppbv, results show that the decrement of $R_{NO/NO_2}$ from 10 to 5 can
642 partly offset $NO_2$ exposure but have much less impacts on NO exposure.

643 Although further investigations are still required to provide practical guidelines,
644 this paper is one of the first attempts to quantify how reactive pollutant source
645 locations and reactant proportions influence reactive pollutant exposure in 3D urban
646 districts, which can present meaningful references for urban planning. The effective
647 methodologies are proposed for reactive pollutant exposure assessment in more
648 complicated urban districts with various meteorological conditions and chemical
649 mechanisms.

650

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**Figure list:**

Fig.1 (a) The population census data of Hong Kong [4]; (b) Time activity patterns for each subgroup in four microenvironments [70].

Fig.2 (a) Idealized 3D urban district models ($H/W$=1, $\lambda_p$=$\lambda_f$=0.25); (b) Computational domains and boundary conditions for test cases; (c) The overhead and lateral views of mesh distribution.

Fig.3 Model setups of vehicular emission sources: (a) S3, (b) S10 and (c) Sm.

Fig.4 (a-b) The side and top views of measured points and model configurations in wind tunnel experiment [87]; (c) Computational domains and boundary conditions in CFD validation study; (d) The mesh arrangements in grid sensitivity test.

Fig.5 Results of grid independence test: (a) $\overline{u}(z)$, (b) $\overline{w}(z)$ at Point V1; Comparison of vertical profiles between wind tunnel data and CFD results: (c-e) $\overline{u}(z)$ at Points V1, V4 and V6, respectively; (f-g) $\overline{w}(z)$ and $k(z)$ at Point V1.

951 Fig.6 (a-b) The lateral and overhead views of experiment settings in concentration
952 measurement [92]; (c) CFD setups in passive dispersion validation; (d-f) Vertical
953 profiles of stream-wise velocity, turbulence kinetic energy and turbulent
954 dissipation rate in domain inlet.

955 Fig.7 Comparison of $K$ between wind tunnel data and CFD results applying standard
956 $k$-$\varepsilon$ model: (a) on the leeward and windward walls; (b) on the central line of roof
957 surface.

958 Fig.8 (a) Velocity distribution in the pedestrian level of $z$=1.5m; (b-c) Velocity
959 magnitude and 2D streamlines for Street 3 (left) and 10 (right) in the plane of
960 $y$=30m and $z$=1.5m, respectively; (d) 3D streamlines in Street 3 and 10.

961 Fig.9 $NO_2$ concentration distribution between P-type (left or above) and R-type (right
962 or below) cases: (a-b) in the plane of $y$=30m with S3 and S10, respectively; (c-d)
963 in the pedestrian level of $z$=1.5m with S3 and S10, respectively; (e) in the
964 pedestrian level of $z$=1.5m with Sm.

965 Fig.10 (a-b) Photostationary state defect between S3 (left) and S10 (right) cases in
966 $y$=30m and $z$=1.5m, respectively.

967 Fig. 11 $NO_2$ concentration between P-type (left or above) and R-type (right or below)
968 cases: (a-b) on the leeward and windward walls with S3 and S10, respectively; (c)
969 on the entire building walls with Sm.

970 Fig.12 $\langle P\_iF \rangle_B$ curves of NO and $NO_2$ in P-type and R-type cases with various
971 source locations: (a) S3, (b) S10 and (c) Sm, respectively.

Fig. 13 $\langle P\_iF \rangle_B$ curves of (a) $NO_2$ and (b) NO in P-type and R-type cases under four $O_3$ background concentrations ($[O_3]$=1,20,40,100ppbv).

Fig. 14 $\langle P\_iF \rangle_B$ curves of (a) $NO_2$ and (b) NO in P-type and R-type cases with three kinds of NO-$NO_2$ emission ratios.

**Table list:**

Table 1 Time patterns and breathing rates in each subgroup for indoors at home ($j$=1)

Table 2 Summary of all test cases

Table 3 Comparison between wind tunnel experiment and CFD simulation

Table 4 $\langle P\_iF \rangle_W$ (unit: ppm) at leeward and windward walls adjoining the target street in S3 and S10 cases

Table 5 $\langle P\_iF_t \rangle_B$ values and the exponential factor $b$ in S3 and S10 cases